



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01J 37/03, 37/02, 13/00	A1	(11) International Publication Number: WO 96/17685 (43) International Publication Date: 13 June 1996 (13.06.96)
(21) International Application Number: PCT/EP95/04803 (22) International Filing Date: 7 December 1995 (07.12.95) (30) Priority Data: P 44 43 705.6 8 December 1994 (08.12.94) DE (71) Applicant (for all designated States except US): STUDIENGESELLSCHAFT KOHLE MBH [DE/DE]; Kaiser-Wilhelm-Platz 1, D-45470 Mülheim (DE). (72) Inventors; and (75) Inventors/Applicants (for US only): BÖNNEMANN, Helmut [DE/DE]; Studiengesellschaft Kohle mbH, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim (DE). BRIJOUX, Werner [DE/DE]; Studiengesellschaft Kohle mbH, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim (DE). BRINKMANN, Rainer [DE/DE]; Studiengesellschaft Kohle mbH, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim (DE). RICHTER, Joachim [DE/DE]; Im Tal 99, D-45529 Hattingen (DE). (74) Agents: JÖNSSON, Hans-Peter et al.; Deichmannhaus am Hauptbahnhof, D-50667 Köln (DE).		(81) Designated States: AL, AM, AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LR, LS, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PROCESS FOR PRODUCING TENSIDE-STABILIZED COLLOIDS OF MONO- AND BIMETALS OF THE GROUP VIII AND IB OF THE PERIODIC SYSTEM IN THE FORM OF PRECURSORS FOR CATALYSTS WHICH ARE ISOLABLE AND WATER SOLUBLE AT HIGH CONCENTRATION		
(57) Abstract <p>The invention relates to a process for producing tenside-stabilized colloids of mono- and bimetals of the group VIII and Ib of the periodic system which are isolable in the form of powder and which are soluble at a concentration of at least 100 mg atom of metal/l of water, from metal salts in the presence of strongly hydrophilic tensides with hydrotriorganoborates in THF, or with simple chemical reduction agents like hydrogen or alkali formate in water and alcohols, respectively. Furthermore, the subject matter of the invention is the use of the tenside-stabilized colloids which are produced according to this process as precursor for supported catalysts for the selective cis-hydrogenation of C-C triple bonds, for the selective hydrogenation of functional groups at the aromatic nucleus, for the selective hydrogenation of benzene to cyclohexene, for the partial oxidation of the primary alcohol functionality in carbohydrates, as well as for use as a precursor for electrocatalysts in fuel cells.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

Process for producing tenside-stabilized colloids of mono- and bimetals of the group VIII and Ib of the periodic system in the form of precursors for catalysts which are isolable and water soluble at high concentration

Summary

The invention relates to a process for producing tenside-stabilized colloids of mono- and bimetals of the group VIII and Ib of the periodic system which are isolable in the form of powder and which are soluble at a concentration of at least 100 mg atom of metal/l of water, from metal salts in the presence of strongly hydrophilic tensides with hydrotriorganoborates in THF, or with simple chemical reduction agents like hydrogen or alkali formate in water and alcohols, respectively. Furthermore, the subject matter of the invention is the use of the tenside-stabilized colloids which are produced according to this process as precursor for supported catalysts for the selective cis-hydrogenation of C-C triple bonds, for the selective hydrogenation of functional groups at the aromatic nucleus, for the selective hydrogenation of benzene to cyclohexene, for the partial oxidation of the primary alcohol functionality in carbohydrates, as well as for use as a precursor for electrocatalysts in fuel cells.

Description of the process

The use of colloiddally stabilized one- and multi-metallic nanoparticles as separately isolable precursor for producing supported metal catalysts is a new, economically beneficial alternative to the traditional in situ formulation of active

- 2 -

metal components on carrier surfaces (H. Bönemann et al., J. Mol. Catal. 86 (1994), 129-177]. The particular characteristic of the process according to the invention is the pre-formation of colloidally stabilized metal nanoparticles, optionally having an intermetallic composition, with defined size and particle structure. The characteristics of the catalyst (activity, selectivity, lifetime) of such metal colloids which are fixed on carriers are superior to conventional, supported catalysts.

The preferred solvent in this catalyst technology is water, due to economical and ecological reasons. The subject matter of the present invention is a process which permits to stabilize mono- and bimetallic nanoparticles in the form of powder in such a way, that highly concentrated colloidal solutions of the corresponding mono- and bimetallic catalyst-precursor can be produced in water without appreciable metal precipitations. By fixation of the precursor from aqueous solution on organic or inorganic carrier materials, new heterogeneous catalysts are prepared according to the invention, for. e.g. selective hydrogenations, partial oxidations, or electrocatalysts for fuel cells.

According to the state of the art, some nanometals can be stabilized colloidally in water [T. Sato, S. Kuroda, A. Takami, Y. Yonezawa, H. Hada, Appl. Organomet. Chem. 1991, 5, 261; T. Sato et al., J. Appl. Phys. 1990, 68, 1297; T. Sato et al., J. Chem. Soc., Faraday Trans. 1, 1987, 83, 1559; T. Sato, S. Kuroda, A. Takami, Y. Yonezawa, H. Hada, Appl. Organomet. Chem. 1991, 5, 261; J. H. Fendler, "Membrane-Mimetic Approach to Advanced Materials", Springer-Verlag, Berlin, 1994; J. S. Bradley in "Clusters and Colloids", (Ed. G. Schmid), VCH, Weinheim 1994; H. Hirai, Y. Nakao, N. Toshima, Chem. Lett. 1978, 5, 545; M. Ohtaki, M. Komiyama, H. Hirai, N. Toshima, Macromolecules 1991, 24, 5567; N. Toshima et al., J. Phys. Chem., 1991, 95, 7448; N. Toshima, T. Yonezawa, Makromol. Chem., Macromol. Symp., 1992,

- 3 -

59,327; N. Toshima et al., J. Phys. Chem. 1992, 96,9927; K. Torigoe, K. Esumi, Langmuir 1993, 9, 1664; J. S. Bradley et al., Chem. Mater. 1993, 5, 254; H. Hirai, Y. Nakao, N. Toshima, Chem. Lett. 1976, 9,905; M. Ohtaki, M. Komiyama, H. Hirai, N. Toshima, Macromolecules 1991, 24,5567, N.Toshima, M. Ohtaki, T. Teranishi, Reactive Polym. 1991, 15, 135; C. Larpent, F. Brisse-Le Menn, H. Patin, Mol. Catal. 1991, 65, L35; N. Toshima, T. Takahashi, Bull. Chem. Soc. Jpn. 1992, 65, 400-9].

However, the described metal colloids cannot be isolated, and they are soluble in water only at a high dilution. Therefore, they are not suitable as a catalyst precursor.

Some authors could isolate water soluble nanometal colloids in the presence of hydrophilic P- and N-donators [J. S. Bradley in "Clusters-and Colloids", (Ed. G. Schmid), VCH, Weinheim 1994; G. Schmidt, Chem. Rev. 1992, 92, 1709, H. Liu, N. Toshima, J. Chem. Soc., Chem. Commun. 1992,1095; C. Amberger, Ber. 1904, 37,124; C. Paal, C. Amberger, Ber. 1905, 38,1398].

Since P- and N-donators, being Lewis bases, give defined metal complex compounds with transition metals which, as is generally known, affects the catalytic efficiency of metals, the use of the mentioned complexing agent for the production of water soluble catalyst precursors is not suitable in the meaning of the present invention. Furthermore, the synthesis of these complexing agents occurs in several steps, and it is uneconomical.

Suitable auxiliary agents are known for stabilizing nanometals in water. Referring to this, also surface-active agents (tensides) were proposed by some authors [H. G. Petrow and R. J. Allen (Prototech Company), US-C 4,044,193 (1977); G. V. Lisichkin, A. Ya. Yuffa and V. Yu. Khinchagashvii, Russ. J. Phys. Chem., 50 (1976) 1285; V. M. Deshpande, P. Singh and C. S.

- 4 -

Narasimhan, J. Mol. Cat., 53 (1989) L21; V. M. Deshpande, P. Singh and C. S. Narasimhan, J. Mol. Cat., 63 (1990) L5; V. M. Deshpande, P. Singh and C. S. Narasimhan, J. Chem. Soc., Chem. Commun., 1990, 1181; Y. Nakao and K. Kaeriyama, J. Coll. and Surf. Sci., 110(1) (1986) 82; C. Larpent, F. Brisse-Le Menn und H. Patin, New J. Chem. 15 (1991) 361; K. Esumi, M. Shiratori, H. Ihshizuka, T. Tano, K. Torigoe and K. Meguro, Langmuir 7 (1991) 457; N. Toshima, T. Takahashi und H. Hirai, Chemistry Letters, 1985, 1245; N. Toshima and T. Takahashi, Chemistry Letters, 1988, 573; J. Kiwi and M. Grätzel, J. Am. Chem. Soc. 101 (1979), 7214]. However, the colloidal solutions of the corresponding metals in water are only stable at an extremely low concentration, not isolable and therefore, are discarded from the beginning as being used according to the invention as precursors for technical catalysts.

A significant progress in the production of water soluble metal colloids received Reetz and Helbig [M.T. Reetz, W. Helbig, J. Am. Chem. Soc. 1994, 116, 7401] by use of a LiCl salt of the sulfobetaine 3-(dimethyldodecyl-ammonio)propane sulfonate in an electrochemical reduction process. According to this electrochemical process, e.g., a good water soluble palladium colloid which is stabilized with sulfobetaine having a size of 8 nm, was isolated.

An economical alternative to the electrochemical production of nanometals is the chemical reduction of metal salts [H. Bönemann et al., Angew. Chem. Int. Ed. Engl. 29 (1990), 273; H. Bönemann et al., J. Mol. Catal. 86 (1994), 129-177].

The use of commercial tensides for the stabilization of chemically-reductively produced nanometal colloids in highly concentrated aqueous solution could not be learned from the state of the art and from the ruling doctrine. On the contrary, surface-active substances are considered as auxiliary agents for

- 5 -

the precipitation of metals from aqueous solution. Surprisingly, it was found now that the chemical reduction of metal salts in the presence of extremely hydrophilic tensides leads to isolable nanometal colloids which form in an amount of at least 100 mg atom metal/l long-term stable solutions in water. The advantage according to the invention of extremely water soluble tensides for the stabilization of colloids illustrates the following comparison: Whereas the poor water soluble tenside $C_{16}H_{33}Me_3NBr$ (solubility according to Fluka catalogue 1993/94, CAS No. 57-09-0 = 0,1 mole/l of water) does not allow a stabilization of metal colloids in water according to the state of the art [G.V. Lisichkin, A.Ya. Yuffa and V.Yu. Khinchagashvii, Russ. J. Phys. Chem., 50 (1076), 1285], the use according to the invention of 3-(dimethyldodecyl-ammonium)propane sulfonate (solubility according to Fluka catalogue 1993/94, CAS No. 14933-08-5 = 1,2 mole/l of water) results in a solubility of the stable metal colloids of at least 100 mg atom/l of water.

Inorganic or organic salts of one or more metals from the groups VIII and Ib of the periodic system are dissolved, respectively suspended, in water or in a strongly solvated organic solvent (ether, THF, alcohols) in the presence of an extremely hydrophilic tenside, and they are reacted between 0°C and 100°C at environmental pressure, optionally by addition of alkali carbonate, with chemical reduction agents. Such reduction agents are, e.g., hydrogen, alkali formate, complex hydrides and other materials which are technically available for the reduction. The selection of the reducing agent will be determined, respectively, according to the reducing capacity which is necessary for the respective metal salt, as well as according to the stability of the used reagents in protic/aprotic solvents. As the extremely hydrophilic tensides, according to the invention, the following hydrophilic types of tensides can be used for the chemically-reductive preparation of colloids of mono- and bimetals of the groups VIII and Ib of the periodic

- 6 -

system in the form of isolable powders which are water soluble in high concentration (> 100 mg atom/l): amphiphilic betaines (A), cationic tensides (B), fatty alcohol-polyglycolether (C), polyoxyethylene-carbohydrate-fatty alkylester (D), anionic tensides (E) and amphiphilic sugar tensides (F).

(The metal colloids which are prepared according to the invention as catalyst-precursor can be raised from aqueous solution to organic or inorganic carrier materials (e.g. activated carbon, graphitized carbon black, metal oxides) for the production of technically advantageously mono- and bimetallic heterogeneous catalysts. These heterogeneous catalysts which are prepared according to the invention are suitable for the selective cis-hydrogenation of C-C triple bonds (mono- and bimetallic Pd-colloidal catalysts on A-carbon), the selective hydrogenation of functional groups, as for instance $-\text{NO}_2$, at the aromatic nucleus (e.g. mono- and bimetallic Pt-colloid on A-carbon), for the selective hydrogenation of benzene to cyclohexene (e.g., Ru-colloid on La_2O_3), for the partial oxidation of the primary alcohol functionality in carbohydrates (e.g., Pd-, Pt-, Pd/Pt-colloids on A-carbon), or as electrocatalysts for fuel cells (e.g., Pt-colloid on graphitized carbon black).

Examples

The following types of tensides can be used according to the invention for the nanometal stabilization (table 1). The examples illustrate the invention without being limited thereby.

- 7 -

Table 1

hydrophilic type of tenside	name	tenside	name, formula, <i>commercial name</i>
A	amphiphilic betaines	A1	3-(N,N-dimethyldodecylammonio)-propane sulfonate (<i>SB12</i>)
		A2	Lauryldimethyl carboxymethyl-ammonium-betaine, <i>REWO</i>
		A3	Cocoamidopropyl betaine, <i>DEHYTON K</i> ,
		A4	Cocoamidopropyl betaine, <i>AMPHOLYT JB130</i> ,
B	cationic tensides	B1	$\begin{array}{c} \text{C}_{18}\text{H}_{37} \quad \text{OH} \quad \text{Cl} \\ \quad \quad \quad \\ \text{Cl}^- \text{CH}_2 - \text{N}^+ - \text{CH}_2 - \text{CH} - \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$ <p><i>QUAB 426</i></p>
		B2	$\begin{array}{c} \text{O} \\ \\ (\text{R} \text{COCH}_2\text{CH}_2)_n \text{N}^+ (\text{CH}_2\text{CH}_2\text{OH})_{3-n} \\ \\ \text{CH}_3 \end{array}$ <p>R = alkyl radical of partially hydrogenated palm grease <i>ESTERQUAT AU35</i></p>
C	fatty alcohol-polyglycolether	C1	polyoxyethylene laurylether, <i>BRIJ 35</i>
D	Polyoxyethylene carbohydrate-fatty alkylester	D1	polyoxyethylene sorbitan monolaurate, <i>TWEEN 20</i>
E	anionic tensides	E1	Na-cocoamidoethyl-N-hydroxyethyl glycinate, <i>DEHYTON G</i>
F	amphiphilic sugar tensides	F1	alkylpolyglycoside, <i>APG 600</i>

- 8 -

Tenside-stabilized colloids of metals of the groups VIII and Ib of the periodic system by reduction with alkali BEt_3H in THF (see table 2).

Example 1

Ru-colloid (table 2, No. 4)

2.43 g (7.23 mmole) 3-(N,N-dimethyldodecylammonium)-propane sulfonate (tenside A1) are suspended under protective gas (argon) in 100 ml THF, and 5.60 ml of a 1,29 molar LiBEt_3H solution in THF is added thereto at 20°C, whereby a clear tenside-reduction agent-solution results. This clear tenside-reduction agent-solution is dropped within 4 h at 40°C under stirring to a suspension of 0.5 g (2.41 mmole) RuCl_3 in 100 ml THF, and stirring is continued for further 16 h at 20°C. A grey-black precipitate and an almost colorless, supernatant solution are formed. After 2 h of settling, the supernatant solution is siphoned off, 5 ml acetone and 100 ml THF are added. It is stirred for about 10 min, and again the precipitate is allowed to settle during 1 h. The supernatant clear solution is siphoned off, and the precipitate is dried in high vacuum (10^{-3} mbar, 40°C, 1h). 0,65 g Ru-colloid in the form of a black solid having a Ru-content of 12.62% are obtained. Particle size according to TEM (transmission electron microscopy): 1-2 nm.

Physical characterization:

The colloids from experiments No. 5 and 26, table 2, were characterized by means of UV spectroscopy.

The XPS-spectrum of colloid No. 19, table 2 shows metallic platinum. The mean particle size was determined by means of TEM of the following colloids: No. 19: 2 nm; No. 20: 2,8 nm; No. 21: 3,7 nm (table 2).

Tenside-stabilized colloids of bimetals of the groups VIII and Ib of the periodic system by reduction with alkali BEt_3H in THF (see table 3).

- 9 -

Example 2

Pt-Co-colloid (table 3, No. 3)

2.62 g (7.8 mmole) 3-(N,N-dimethyldodecylammonium)-propane sulfonate (tenside A1) are suspended under protective gas (argon) in 100 ml THF, and 6 ml of a 1,29 molar LiEt_3H solution in THF is added thereto at 20°C, whereby a clear tenside-reduction agent-solution results. This clear tenside-reduction agent-solution is dropped within 20 h at 20°C under stirring to a suspension of 0.78 g (2.93 mmole) PtCl_2 and 0.13 g (0.98 mmole) CoCl_2 in 120 ml THF, and stirring is continued for further 67 h at 20°C. A dark grey-brown precipitate is formed. 10 ml acetone are added, it is stirred for 1 h, and the precipitate is allowed to settle. The supernatant clear solution is siphoned off, and the precipitate is washed twice with 50 ml THF. After drying in high vacuum (10^{-3} mbar, 20°C, 1h) 2,84 g Pt-Co-colloid in the form of a black solid having a metal content of 17.6% Pt and 1,5% Co is obtained. Particle size according to TEM: 2-6 nm.

Physical characterization:

The colloids from experiments No. 4 and 6, table 3, were characterized by means of UV spectroscopy.

Tenside-stabilized colloids of metals of the groups VIII and Ib of the periodic system by reduction with alkali metal boron hydrides in H_2O and alcohols, respectively (see table 4).

Example 3

Pt-colloid (table 4, No. 7)

2.7 g (5.3 mmole) $\text{H}_2\text{PtCl}_6 \times 6 \text{ H}_2\text{O}$ and 3.6 g (10.6 mmole) 3-(N,N-dimethyldodecylammonium)propane sulfonate (tenside A1) are dissolved under the protective gas argon in 100 ml H_2O , and within 2 h a solution of 1.2 g (31.8 mmole) NaBH_4 in 50 ml H_2O are added thereto at 20°C. The resultant deep-black reaction mixture is filtered over a D4 glass frit, and the deep-black clear solution is concentrated in high vacuum (10^{-3} mbar, 40°C)

- 10 -

to dryness. 6.39 g Pt-colloid is yielded in the form of a black solid having a Pt content of 12,1%. Mean particle size according to TEM: 4,6 nm.

Physical characterization:

The colloid from experiment No. 2, table 3, was characterized by means of UV spectroscopy.

Tenside-stabilized colloids of bimetals of the groups VIII and Ib of the periodic system by reduction with alkali metal boron hydrides in H₂O and alcohols, respectively (see table 5).

Example 4

Pt-Cu-colloid (table 5, No. 1)

1.35 g (2.65 mmole) H₂PtCl₆ x 6 H₂O and 0.11 g (0.66 mmole) CuCl₂ x H₂O are dissolved with 4.3 g (12.7 mmole) 3-(N,N-dimethyldodecylammonium)propane sulfonate (tenside A1) under protective gas (argon) in 100 ml H₂O, and within 2 h a solution of 0.38 g (17.0 mmole) LiBH₄ in 50 ml H₂O are added thereto at 20°C. The resultant deep-black reaction mixture is filtered over a D4 glass frit, and the deep-black clear solution is concentrated in high vacuum (10⁻³ mbar, 40°C) to dryness. 7.05 g Pt-Cu-colloid is yielded in the form of a black solid having a metal content of 7.02% Pt and 0,52% Cu. Particle size according to TEM: 2.5-4.5 nm; EDX-analysis: Pt:Cu = 1:0.2

Physical characterization:

The particle size of colloid no. 6, table 5 was determined by TEM: 3-5 nm; EDX-analysis: Pt:Ru = 1:1.05

Tenside-stabilized colloids of metals of the groups VIII and Ib of the periodic system by reduction with hydrogen in H₂O (see table 6).

- 11 -

Example 5Pt-colloid (table 6, No. 15)

1.4 g (5.3 mmole) PtCl_2 , 7.2 g (21.2 mmole) 3-(N,N-dimethyldodecylammonium)propane sulfonate (tenside A1) and 0.4 g (5.3 mmole) Li_2CO_3 are taken up under a protective gas (argon) in 100 ml H_2O , and during 3 h a stream of H_2 is passed through this mixture at 20°C . A clear black solution is formed after approximately 30 min, from which all volatile matter is separated in high vacuum (10^{-3} mbar, 40°C). 8.4 g Pt-colloid is yielded in the form of a black solid having a Pt-content of 10.7%. Mean particle size according to TEM: 2.2 nm.

Annotation relating to operating the reaction:

Experiment no. 17, table 6 - deviating from the description of the above experiments - was performed in air.

Physical characterization:

The colloids from experiment nos. 1, 4, 5 and 6, table 6 were characterized by uv-spectroscopy.

The mean particle size of the following colloids was determined by TEM: no. 10:2.2 nm; no. 11:3.1 nm (table 6).

Tenside-stabilized colloids of bimetals of the groups VIII and Ib of the periodic system by reduction with hydrogen in H_2O

Example 6Pt-Pd-colloid

1.35 g (2.65 mmole) $\text{H}_2\text{PtCl}_6 \times 6 \text{H}_2\text{O}$ and 0.7 g (2.65 mmole) $\text{Pd}(\text{NO}_3)_2 \times \text{H}_2\text{O}$ are dissolved together with 7 g polyoxyethylenelauryl ether (tenside C1) and 1.0 g (13.25 mmole) Li_2CO_3 under a protective gas (argon) in 100 ml H_2O , and during 4 h H_2 gas is passed through it at 20°C . The resultant deep black reaction mixture is filtered over a D4 glass frit, and the deep-black clear solution is concentrated in high vacuum (10^{-3} mbar, 40°C)

- 12 -

to dryness. 11,2 g Pt-Pd colloid are obtained in the form of a black solid having a metal content of 4.3% Pt and 2.3% Pd.

Tenside-stabilized colloids of bimetals of the groups VIII and Ib of the periodic system by reduction with Li-formate in H₂O

Example 7

Pt-Rh-colloid

1.35 g (2.65 mmole) H₂PtCl₆ x 6 H₂O and 0,7 g (2.65 mmole) RhCl₃ x H₂O are dissolved with 7 g polyoxyethylene laurylether (tenside C1) under a protective gas (argon) in 150 ml H₂O, and during 20 h a solution of 2.86 g (55.0 mmole) Li-formate in 50 ml H₂O is added thereto at 60°C. The resultant deep black reaction mixture is filtered over a D4 glass frit, and the deep-black clear solution is concentrated in high vacuum (10⁻³ mbar, 40°C) to dryness. 12.5 g Pt-Rh colloid are obtained in the form of a black solid having a metal content of 4.0% Pt and 2.0% Rh.

Fixation of the carrier

Example 8

Preparation of a Pd-tenside Al/activated carbon catalyst for the partial oxidation of carbohydrates (5 percent per weight of Pd/C)

1.254 g of a microporous (< 5nm) powdery active carbon having a grain size of 20 µm are suspended in 50 ml deoxygenated H₂O, and 64.7 ml of a solution of Pd-colloid no. 16, table 2 in deoxygenated water (1.02 mg Pd/ml) are given thereto within 16 h under stirring. The covered active carbon is separated over a glas filter frit; yielding a colorless filtrate. It is washed twice with 25 ml deoxygenated water, respectively, and dried during 16 h in vacuum (10⁻³ mbar). Subsequently, the catalyst is oxygenated during 16 h at 0,1 mbar (approximately 0,2% O₂). The obtain d catalyst can be handled in air.

- 13 -

Example 9

Preparation of a Pd-tenside Al/active carbon-catalyst for the selective hydrogenation of $C\equiv C$ (5% per weight of Pd/C)

A solution of 0.7885 g (corresponding to 0.1053 g Pd) colloid no. 16, table 2 in 40 ml distilled water is dropped within 16 h under argon to 2.00 activated carbon (Degussa carrier material 101, charge 514) which was given in the form of a suspension in 40 ml water under argon. Thereby, the colloid is completely absorbed on the activated carbon which can be seen by the decoloration of the solution. The catalyst is filtered off, dried during 16 h at 20°C in high vacuum (10^{-3} mbar), and it is oxygenated during 16 h at 20°C at 0.1 mbar (approximately 0.2% O_2).

Example 10

Preparation of a Ru-tenside Al/lanthanumoxid catalyst for the selective hydrogenation of benzene (1 percent per weight of Ru/La₂O₃).

5.505 g La₂O₃ (BET surface area of 59 m²/g) are suspended in 100 ml deoxygenated H₂O under a protective gas. Within 30 min 50 ml of a solution of Ru-colloid no.4, table 2 in deoxygenated H₂O (440 mg, EA: 12.62% Ru), is dropped thereto. Thereby, the white oxidic carrier changes to a grey colour. The complete absorption can be seen from the decoloration of the black solution. The coated carrier is allowed to settle completely, and the supernatant, clear aqueous solution is siphoned off. After drying in vacuum (10^{-3} mbar, 3 h), a grey powder is obtained which is stable in air.

Catalysis

Example 11

Use of a Pd-catalyst for the oxidation of glucose to gluconic acid.

100 ml of an aqueous solution of glucose with 16 g glucose (99 percent per weight) (88 mmole) and 0.24 g of the catalyst described in example 8 (1.5 percent per weight in relation to the amount of glucose) are transferred to a 250 ml stirring reactor equipped with gassing stirrer, thermometer, alkali metering, pH electrode and oxygen feeding. The oxygen is distributed at normal pressure by means of the gassing stirrer in the solution at a reaction temperature of 56°C. The resulting gluconic acid is neutralized by dropping 10 percent per weight of caustic soda thereto. Thereby, the pH value of the suspension is 10.0. The catalyst is filtered off, and the filtrate is analyzed by means of ion chromatography and HPLC.

Conversion (min): 49%

Selectivity (120 min): 92%

Activity (120 min): 327 g [gluconic acid]/g [Pd] x hour

Example 12

Use of a Pd-catalyst for the selective hydrogenation of 3-hexyne-1-ol to cis-3-hexene-1-ol

30.0 mg of a Pd-colloid/activated carbon catalyst, prepared according to example 9, are weighed in a 100 ml dropping funnel. The measuring of the selectivity is performed in a reactor which is thermostatted to -10°C. The dropping funnel is put upon the reactor, the whole apparatus is evacuated several times and flushed with hydrogen. Subsequently, the catalyst is placed into the reactor in hydrogen-counterflow with 100 ml of absolute, non-degenerated ethanol under argon in 2 portions of 50 ml, respectively. The dropping funnel is taken off and it is replaced by a septum. 10 ml 3-hexyne-1-ol are injected through the septum. After thermostating the suspension at -10°C and

- 15 -

pressure compensation, the path to a 1 l-precision buret which is sealed by mercury is opened. GC samples are taken through the septum by means of a syringe with filter aid and hypodermic steel needle in regular intervals until stoichiometric hydrogen take-up is attained. Selectivity according to GC: 94.9%.

Example 13

Use of a Ru-catalyst for the partial hydrogenation of benzene to cyclohexene

10 ml benzene, 40 ml water with 3 g NaOH and 500 mg of the catalyst described in example 10 (1 percent per weight Ru/La₂O₃, 6.25 percent per weight of catalyst in relation to the amount of benzene) are filled into a 100 ml stainless steel autoclave. The content is stirred with the club stirrer and heated to 150°C. Now, it is pressed on to 50 bar of hydrogen pressure. The autoclave is taken from the heating jacket support after 30 min, and stirring is interrupted. Thereby, a hydrogen up-take of 18 bar can be noticed. The residual H₂ pressure is blown off after cooling, and a sample is taken from the upper organic phase which is examined by gas chromatography.

Conversion(benzene): 8.5%

Selectivity (cyclohexene): 78.5%.

Example 14

Preparation of a platinum colloid stabilized by dihydrocinchonidine

0.104 g PtCl₄ (0.31 mmole) are dissolved in a 100 ml two-neck flask, provided with reflux condenser and a septum, in 83 ml water, and heated to reflux temperature in an oil bath. The temperature of the oil bath is 140°C (±5°C) during the synthesis. A solution of 0.092 g dihydrocinchonidine (0.31 mmole) in 7 ml of 0.1 n. formic acid is rapidly injected through the septum. In the beginning, the reaction mixture becomes turbid and begins to become black colored after some minutes. The reaction is finished approximately ten minutes after the

- 16 -

beginning of the black coloration. The reaction mixture is frozen in liquid nitrogen and liberated of water and the forming hydrochloric acid by freeze drying. A black powder is obtained which can be completely dispersed in water. If the formed platinum colloids should be applied on carrier materials, the aqueous product dispersion can be used without isolation of the metal particles before the application on the carrier. The yield is 0.18 g (103% of the theory) in this reaction. The elemental analysis shows 34.5% Pt, 16% Cl, 39.5% C, 5% H and 5% N. Electron-microscopic examinations show an average particle size of 2 nm.

Example 15

Preparation of a heterogeneous platinum catalyst by adsorption of platinum colloids on silicon dioxide and active carbon

100 ml of the colloid, described in example 14, are directly taken up after the synthesis in 100 ml cold, distilled water, and are dropped during one hour to 100 ml of the carrier suspension. Either the highly disperse silicon dioxide Aerosil P 25TM (Degussa) or the active carbon carrier 196 (Degussa) which was oxidized with sodium hypochloride before the application to the carrier, can be used as carriers. The obtained suspensions are stirred with a magnetic stirrer at a low rotational speed during two days, and they are subsequently filtrated. The filtrate is completely discolored, a fact from which it can be concluded that the metal colloids were quantitatively absorbed on the carrier. The thus obtained heterogeneous platinum catalysts were dried in a drying oven, and they can be used subsequently as hydrogenation catalysts without further intermediary step. A uniform and agglomeration-free distribution of the colloids on the carrier materials could be proven by electron-microscopic examinations.

- 17 -

Example 16

Enantioselective hydrogenation of 2-keto-propane acid ethylester to 2-hydroxy-propane acid ethylester

A 100 ml autoclave is charged with the catalyst described in example 15 (platinum on silicon dioxide; metal content 5%), 5 ml 2-keto-propane acid ethylester (45 mmole), 20 ml dihydrocinchonidine (0.1 mmole), 10 ml acetic acid and a magnetic stirrer nucleus having a size of 3 cm. The pressure vessel is degassed after being closed, and subsequently, 100 bar hydrogen are pressed on under vigorous stirring. The reaction takes place at 20°C, and it is terminated approximately after 15 minutes. Following the expansion of the pressure vessel, the product mixture is liberated of the catalyst by filtration, the clear filtrate is taken up in 180 ml saturated sodium bicarbonate solution and subsequently extracted three times with each 20 ml of diethyl ether. The combined organic phases are concentrated on a rotary evaporator, the remaining clear solution is examined by NMR spectroscopy and mass spectroscopy, and it is identified as 2-hydroxy-propane acid ethylester. The yield was determined by gas chromatography to 90%. The optical yield of the reaction was examined by gas chromatography on a chiral column, and yields an excess of enantiomer of 81%.

Table 2: Tenside-stabilized colloids of metals of the groups VIII-Ib of the periodic system by reduction with alkali BEt_3H in THF

No.	Metal:salt	Tenside	Metal salt/- tenside	Reduction agent	Solvent	Reaction conditions	isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmmole	g/mmmole	molar ratio	mmole	ml	T, °C	t, h	%	
1	NiBr ₂	C1	-	LiBEt ₃ H	THF	50	20	Ni: 2,9	110
	0,7/5,3	7/-		10,6	200				
2	CoCl ₂	C1	-	LiBEt ₃ H	THF	50	20	Co: 3,1	120
	0,7/5,3	7/-		10,6	200				
3	CuCl ₂	A1	1:4	LiBEt ₃ H	THF	20	48	Cu: 3,5	300
	0,71/5,3	7,2/21,2		10,6	500				
4	RuCl ₃	A1	1:3	LiBEt ₃ H	THF	40	4	Ru: 12,62	310
	0,5/2,41	2,43/7,23		7,23	200				
5	RuCl ₃	A2	1:3	LiBEt ₃ H	THF	40	2	Ru: 13,52	150
	0,21/1,04	0,85/3,13		3,13	100				
6	RhCl ₃	A1	1:3	LiBEt ₃ H	THF	65	28	Rh: 25,21	320
	2,05/9,7	9,86/29,38		30,78	600				
7	RhCl ₃	A1	1:2	LiBEt ₃ H	THF	40	34	Rh: 11,50	350
	0,45/2,15	1,443/4,3		6,45	105				
8	RhCl ₃	A1	1:1	LiBEt ₃ H	THF	40	34	Rh: 20,4	370
	0,45/2,15	0,721/2,15		6,45	105				

Table 2: continuation 1

No.	Metal salt g/mmmole	Tenside g/mmmole	Metal salt/ tenside molar ratio	Reduction agent mmole	Solvent ml	Reaction conditions T, °C	t, h	isolated amount of product g	Metal content %	Water solubility in mg atom metal / l water
9	RhCl ₃	A1	1:0,75	LiBEt ₃ H	THF	40	34	0,87	Rh: 25,2	410
	0,45/2,15	0,541/1,61		6,45	105					
10	RhCl ₃	A1	1:0,5	LiBEt ₃ H	THF	40	34	0,67	Rh: 32,9	440
	0,45/2,15	0,361/1,075		6,45	105					
11	RhCl ₃	A2	1:3	LiBEt ₃ H	THF	60	16	2,0	Rh: 10,1	180
	0,45/2,15	1,745/6,45		6,45	120					
12	RhCl ₃	A2	1:2	LiBEt ₃ H	THF	60	16	1,60	Rh: 13,1	170
	0,45/2,15	1,164/4,3		6,45	120					
13	RhCl ₃	A2	1:3	LiBEt ₃ H	THF	60	16	2,0	Rh: 10,1	140
	0,45/2,15	1,745/6,45		6,45	120					
14	RhCl ₃	A3	1:2	LiBEt ₃ H	THF	60	16	1,30	Rh: 16,2	110
	0,45/2,15	0,855/4,3		6,45	120					
15	PdCl ₂	A2	1:2	LiBEt ₃ H	THF	25	16	2,64	Pd: 14,8	160
	0,71/4	2,17/8		5,6	300					
16	PdCl ₂	A1	1:2	LiBEt ₃ H	THF	25	16	3,13	Pd: 13,35	280
	1,37/7,75	5,2/15,5		10,8	500					

Table 2, continuation 2

No.	Metal salt	Tenside	Metal salt/ tenside	Reduction agent	Solvent	Reaction conditions	isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio	mmole	ml	T, °C	t, h	%	
7	PdCl ₂	A1	1:2	LiBEt ₃ H	THF	25	24	Pd: 13,7	260
	0,71/4	2,68/8		5,6	300				
8	IrCl ₃	A1	1:3	LiBEt ₃ H	THF	60	16	Ir: 8,99	370
	0,51/1,71	1,72/5,13		5,16	100				
9	PtCl ₂	A1	1:2	LiBEt ₃ H	THF	20	24	Pt: 58,93	420
	2,74/10,3	6,94/20,68		20,69	1100				
20	PtCl ₂	A1	1:1	LiBEt ₃ H	THF	20	27	Pt: 32,64	350
	1,03/3,87	1,31/3,9		7,74	240				
21	PtCl ₂	A1	1:0,5	LiBEt ₃ H	THF	20	27	Pt: 51,50	320
	1,03/3,87	0,655/1,95		7,74	240				
22	PtCl ₂	A2	1:2	LiBEt ₃ H	THF	25	16	Pt: 22,09	160
	5,5/20,67	11,3/41,7		41,7	1200				
23	PtCl ₂	A2	1:1	LiBEt ₃ H	THF	20	16	Pt: 22,6	170
	0,133/0,5	0,138/0,5		1,0	80				
24	PtCl ₂	A2	1:0,5	LiBEt ₃ H	THF	20	16	Pt: 27,7	180
	0,133/0,5	0,068/0,25		1,0	80				

Table 2: continuation 3

No.	Metal salt	Tenside	Metal salt/- tenside	Reduction agent	Solvent	Reaction conditions	isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio	mmole	ml	T, °C	t, h	%	
25	PtCl ₂	A3	1:2	LiBEt ₃ H	THF	20	108	Pt: 19.60	110
		0.857/3.23	2.35/6.45	6.45	200				
26	AgBr	A1	1:2	LiBEt ₃ H	THF	20	24	Ag: 11.52	130
		1.36/5.1	3.5/10.2	10.2	550				

Table 3. Tenside-stabilized colloids of bimetals of the groups VIII-Ib of the periodic system by reduction with alkali BEt_3H in THF

No	Metal salt	Tenside	Metal salt/-tenside	Reduction agent	Solvent	Reaction conditions	isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio	mmole	ml	T, °C, t, h	g	%	
1	$\text{RuCl}_3 \cdot \text{FeCl}_3$ 0,5/2,41 - 0,039/0,24	A1	1:3	LiBEt_3H 7,95	THF 200	60 4	2,60	Ru: 8,84 Fe: 0,38	210
2	$\text{RuCl}_3 \cdot \text{FeCl}_3$ 0,5/2,41 - 0,078/0,48	A1	1:3	LiBEt_3H 8,67	THF 200	60 4	2,45	Ru: 8,52 Fe: 0,71	170
3	$\text{PtCl}_2 \cdot \text{CoCl}_2$ 0,78/2,93 - 0,13/0,98	A1	1:2	LiBEt_3H 7,74	THF 220	20 20	2,84	Pt: 17,6 Co: 1,5	280
4	$\text{PtCl}_2 \cdot \text{CoBr}_2$ 0,86/3,23 - 0,7/3,2	A2	1:2	LiBEt_3H 12,9	THF 300	20 20	4,18	Pt: 12,4 Co: 3,75	200
5	$\text{PtCl}_2 \cdot \text{CoBr}_2$ 0,86/3,23 - 0,08/0,36	A2	1:2	LiBEt_3H 7,2	THF 300	20 20	3,1	Pt: 20,1 Co: 0,68	210
6	$\text{CoDPICl}_2 \cdot \text{CoBr}_2$ 0,6/1,6 - 0,35/1,61	A2	1:2	LiBEt_3H 6,45	THF 300	20 20	1,92	Pt: 14,5 Co: 4,4	190
7	$\text{PtCl}_2 \cdot \text{NiBr}_2$ 0,68/3,23 - 0,08/0,36	A2	1:2	LiBEt_3H 7,2	THF 300	20 20	3,0	Pt: 20,9 Ni: 0,7	185
8	$\text{PtCl}_2 \cdot \text{RhCl}_3$ 2,31/8,72 - 0,61/2,91	A1	1:2,25	LiBEt_3H 26,16	THF 1200	40 24	2,66	Pt: 43,6 Rh: 7,55	405

Table 3: continuation

No	Metal salt g/mmole	Tenside g/mmole	Metal salt/- tenside molar ratio	Reduction agent mmole	Solvent ml	Reaction conditions T, °C t, h	isolated amount of product g	Metal content %	Water solubility in mg atom metal/l water
9	PtCl ₂ - RhCl ₃ 1,80/6,79 - 1,41/6,74	A1 11,56/34,45	1:2,55	LiBEt ₃ H 34,0	THF 1100	50 28	3,60	Pt: 25,0 Rh: 11,1	380
10	PtCl ₂ - RhCl ₃ 0,88/3,32 - 2,76/13,18	A1 15,5/46,19	1:2,8	LiBEt ₃ H 46,17	THF 1200	60 24	4,4	Pt: 13,89 Rh: 16,3	370
11	PtCl ₂ - PdCl ₂ 1,03/3,88 - 0,68/3,88	A1 5,2/15,5	1:2	LiBEt ₃ H 15,5	THF 550	20 24	5,13	Pt: 8,42 Pd: 4,45	350
12	PtCl ₂ - IrCl ₃ 3,99/15,0 - 0,49/1,67	A1 11,74/35,0	1:2,1	LiBEt ₃ H 35,0	THF 1200	60 16	16,03	Pt: 17,3 Ir: 1,87	430
13	PtCl ₂ - IrCl ₃ 1,86/7,0 - 2,09/7,0	A1 11,74/35,0	1:2,5	LiBEt ₃ H 35,0	THF 1200	60 16	14,4	Pt: 8,8 Ir: 8,6	410
14	PtCl ₂ - IrCl ₃ 0,37/1,4 - 3,76/12,6	A1 13,62/40,6	1:2,9	LiBEt ₃ H 66,4	THF 1200	60 64	18,22	Pt: 1,4 Ir: 13,0	400
15	PtCl ₂ - IrCl ₃ 3,99/15,0 - 0,49/1,67	A2 9,48/35,0	1:2,1	LiBEt ₃ H 39,5	THF 660	60 16	10,65	Pt: 15,3 Ir: 1,6	190

Table 4: Tenside-stabilized colloids of metals of the groups VIII-Ib of the periodic system by reduction with alkali metal boron hydrides in H₂O and alcohols, respectively

No.	g/mmole Metal salt	g/mmole Tenside	Metal salt/ tenside	Reduction agent	Solvent	Reaction conditions	T, °C	t, h	isolated amount of product	Metal content	Water solubility in mg atom metal / l water
				mmole	ml				g	%	
	RuCl ₃ × 3H ₂ O	A1 - NH ₄ Cl	1:3	NaBH ₄	H ₂ O	40	2	2	1,24	Ru: 7,65	430
	0,36/1,74	1,75/5,21 - 0,28/5,21		0,2/5,21	150						
2	RuCl ₃ × 3H ₂ O	A1 - NH ₄ Cl	1:3	LiBH ₄	H ₂ O	40	2	2	0,42	Ru: 9,87	425
	0,31/1,17	1,18/3,51 - 0,19/3,51		0,08/3,51	160						
3	RhCl ₃ × 3H ₂ O	A1 - NH ₄ Cl	1:3	NaBH ₄	H ₂ O	20	2	2	1,14	Rh: 8,25	450
	0,30/1,43	1,44/4,3 - 0,23/4,3		0,17/4,3	100						
4	RhCl ₃ × 3H ₂ O	A1	1:4	LiBH ₄	Ethanol	0	24	24	7,3	Rh: 5,5	110
	1,4/5,3	7,2/21,2		0,34/15,9	150						
5	PtCl ₂	A1	1:4	NaBH ₄	H ₂ O	20	24	24	0,92	Pt: 9,8	355
	0,126/0,48	0,669/1,99		0,037/1,0	80						
6	PtCl ₂	A1 - NH ₄ Cl	1:2	NaBH ₄	H ₂ O	20	3	3	4,8	Pt: 10,2	360
	1,4/5,3	3,6/10,6 - 0,47/9		0,4/10,6	100						
7	H ₂ PtCl ₆ × 6H ₂ O	A1	1:2	NaBH ₄	H ₂ O	20	2	2	6,39	Pt: 12,1	320
	2,7/5,3	3,6/10,6		1,2/31,8	150						
8	H ₂ PtCl ₆ × 6H ₂ O	A1	1:4	LiBH ₄	Ethanol	0	24	24	8,1	Pt: 9,5	120
	2,7/5,3	7,2/21,2		1,2/31,8	150						

Table 5: Tenside-stabilized colloids of bimetals of the groups VIII-Ib of the periodic system by reduction with alkali metal boron hydrides in H₂O and alcohols, respectively

No.	Metal salt	Tenside	Metal salt/- tenside	Reduction agent	Solvent	Reaction conditions	isolated amount of product	Metal content	Water solubility in mg atom metal /l water
	g/mmole	g/mmole	molar ratio	mmole	ml	T, °C	t, h	%	
1	H ₂ PtCl ₆ · CuCl ₂ x H ₂ O	A1	1:3,84	LiBH ₄	H ₂ O	20	2	Pt: 7,02	390
	1,35/2,65 - 0,11/0,66	4,3/12,7		0,38/17,0	150			Cu: 0,52	
2	H ₂ PtCl ₆ · CuCl ₂ x H ₂ O	A2	1:8	LiBH ₄	H ₂ O	20	2	Pt: 6,0	170
	1,35/2,65 - 0,05/0,295	6,4/23,6		0,38/17	150			Cu: 0,2	
3	RhCl ₃ x H ₂ O · IrCl ₃ x H ₂ O	A1	1:4	LiBH ₄	H ₂ O	20	2	Rh: 2,7	340
	0,7/2,65 - 0,8/2,65	7,2/21,2		0,3/13,25	200			Ir: 5,0	
4	RhCl ₃ x H ₂ O · RuCl ₃ x H ₂ O	A1	1:4	LiBH ₄	H ₂ O	20	2	Rh: 2,3	410
	0,7/2,65 - 0,7/2,65	7,2/21,2		0,35/15,9	200			Ru: 2,3	
5	RuCl ₃ x H ₂ O · IrCl ₃ x H ₂ O	A1	1:4	LiBH ₄	H ₂ O	20	2	Ru: 2,6	450
	0,7/2,65 - 0,8/2,65	7,2/21,2		0,35/15,9	200			Ir: 4,9	
6	H ₂ PtCl ₆ · RuCl ₃ x H ₂ O	A1	1:4	LiBH ₄	H ₂ O	20	2	Pt: 4,5	380
	1,35/2,65 - 0,7/2,65	7,2/21,2		0,53/23,85	200			Ru: 2,2	
7	H ₂ PtCl ₆ · RuCl ₃ x H ₂ O	A1	1:4	LiBH ₄	Ethanol	0	24	Pt: 4,7	120
	1,35/2,65 - 0,7/2,65	7,2/21,2		0,53/23,85	200			Ru: 2,3	
8	H ₂ PtCl ₆ · RhCl ₃ x H ₂ O	A1	1:4	NaBH ₄	H ₂ O	20	2	Pt: 4,3	360
	1,35/2,65 - 0,7/2,65	7,2/21,2		0,9/23,85	200			Rh: 2,0	

Table 5: continuation

No	Metal salt	Tenside	Metal salt/- tenside	Reduction agent	Solvent	Reaction conditions	isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio	g/mmole	ml	T, °C t, h	g	%	
8	$H_2PtCl_6 \cdot RhCl_3 \times H_2O$	A1	1:4	LiBH ₄	H ₂ O	20 2	10,58	Pt: 4,5	355
	1,35/2,65 - 0,7/2,65	7,2/21,2		0,53/23,85	200			Rh: 2,2	
10	$H_2PtCl_6 \cdot PdCl_2 \times 2 H_2O$	A1	1:4	LiBH ₄	H ₂ O	20 2	11,1	Pt: 4,5	310
	1,35/2,65 - 1,0/2,65	7,2/21,2		0,47/21,2	150			Pd: 2,5	
11	$H_2PtCl_6 \cdot Pd(NO_3)_2 \times H_2O$	C1		LiBH ₄	H ₂ O	20 2	10,2	Pt: 2,0	140
	0,55/1,06 - 1,1/4,24	7,0/-		0,33/14,8	150			Pd: 4,3	
12	$H_2PtCl_6 \cdot IrCl_3 \times H_2O$	A1	1:4	LiBH ₄	H ₂ O	20 2	10,34	Pt: 4,3	400
	1,35/2,65 - 0,8/2,65	7,2/21,2		0,47/21,2	200			Ir: 4,4	
13	$H_2PtCl_6 \cdot IrCl_3 \times H_2O$	A1	1:4	LiBH ₄	H ₂ O	20 2	10,2	Pt: 4,4	420
	1,35/2,65 - 0,8/2,65	7,2/21,2		0,53/23,85	200			Ir: 4,5	

Table 6: Tenside-stabilized colloid of metals of the groups VIII-Ib of the periodic system by reduction with hydrogen in H₂O

No	Metal salt	Tenside	Metal salt/-tenside molar ratio	Reduction agent	Solvent	Reaction conditions T, °C t, h P, bar	isolated amount of product g	Metal content %	Water solubility in mg atom metal/l water
1	RuCl ₃ ·3H ₂ O	A1	1:3	H ₂	H ₂ O	60 10 1	0,43	10,98	370
	0,25/0,95	0,96/2,89			100				
2	RuCl ₃	A1	1:3	H ₂	H ₂ O	60 16 50	0,22	9,41	375
	0,16/0,78	0,79/2,34			100				
3	RuCl ₃ ·3H ₂ O	A2 - K ₂ CO ₃	1:3	H ₂	H ₂ O	60 3 1	0,38	7,1	160
	0,22/0,84	0,68/2,53 - 0,23/1,67			80				
4	Ru ₂ (OAc) ₄	A1	1:6	H ₂	H ₂ O	60 16 50	0,41	8,78	210
	0,27/0,62	1,25/3,7			100				
5	Ru(Acac) ₃	A1	1:3	H ₂	H ₂ O	60 16 50	0,35	9,37	340
	0,39/0,97	0,98/2,91			100				
6	RhCl ₃ ·3H ₂ O	A1	1:3	H ₂	H ₂ O	20 2 1	1,02	11,40	330
	0,42/1,6	1,62/4,81			60				
7	RhCl ₃ ·3H ₂ O	A2	1:3	H ₂	H ₂ O	20 2 1	0,85	10,73	150
	0,40/1,52	1,24/4,57			100				
8	PdBr ₂	A1 - Li ₂ CO ₃	1:4	H ₂	H ₂ O	20 3 1	9,6	5,3	290
	1,4/5,3	7,2/21,2 - 0,4/5,3			100				

Table 6: continuation 1

No	Metal salt	Tenside	Metal salt/- tenside	Reduction agent	Solvent	Reaction conditions	isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio		ml	T, °C t, h P, bar	g	%	
9	H ₂ PtCl ₆ x 6 H ₂ O	A1 - Na ₂ CO ₃	1:4	H ₂	H ₂ O	20 4 1	12,6	7,1	360
	2,7/5,3	7,2/21,2 - 3,4/31,8			100				
10	PtCl ₂	A1 - K ₂ CO ₃	1:4	H ₂	H ₂ O	20 1,5 1	8,79	9,7	330
	1,4/5,3	7,2/21,2 - 0,73/5,3			100				
11	PtCl ₂	A1 - K ₂ CO ₃	1:4	H ₂	H ₂ O	20 3 1	8,5	10,1	310
	1,4/5,3	7,2/21,2 - 0,73/5,3			100				
12	PtCl ₂	A1 - Na ₂ CO ₃	1:4	H ₂	H ₂ O	20 1,5 1	9,0	10,8	350
	1,4/5,3	7,2/21,2 - 0,56/5,3			100				
13	PtCl ₂	A1 - Li ₂ CO ₃	1:4	H ₂	H ₂ O	20 2 1	140	10,3	370
	21/79,5	108/318 - 6/79,5			1500				
14	PtCl ₂	A1 - Li ₂ CO ₃	1:2	H ₂	H ₂ O	20 2 1	73,7	17,9	450
	21/79,5	54/159 - 3/39,75			1500				
15	PtCl ₂	A1 - Li ₂ CO ₃	1:4	H ₂	H ₂ O	20 3 1	8,4	10,7	380
	1,4/5,3	7,2/21,2 - 0,4/5,3			100				
16	PtCl ₂	A1 - Li ₂ CO ₃	1:2	H ₂	H ₂ O	20 2 1	6,1	16,4	440
	1,4/5,3	3,6/10,6 - 0,2/2,65			100				

Table 6: continuation 2

No	Metal salt	Tenside	Metal salt/ tenside	Reduction agent	Solvent	Reaction conditions	Isolated amount of product	Metal content	Water solubility in mg atom metal / l water
	g/mmole	g/mmole	molar ratio		ml	T, °C t, h P, bar	g	%	
17	PtCl ₂	A1 - Li ₂ CO ₃	1:4	H ₂	H ₂ O	20 1,5 1	9,5	10,4	380
	1,4/5,3	7,2/21,2 - 0,4/5,3			100				
18	PtCl ₂	A1 - LiBr	1:4	H ₂	H ₂ O	20 3 1	9,7	9,8	360
	1,4/5,3	7,2/21,2 - 0,5/5,3			100				
19	PtCl ₂	A1 - LiBr	1:2	H ₂	H ₂ O	20 3 1	6,1	16,9	370
	1,4/5,3	3,6/10,6 - 0,25/2,65			100				
20	PtCl ₂	A2 - Li ₂ CO ₃	1:8	H ₂	H ₂ O	20 3 1	14,1	7,1	160
	1,4/5,3	11,5/42,4 - 0,8/10,6			100				
21	PtCl ₂	A4 - Li ₂ CO ₃	1:8	H ₂	H ₂ O	20 3 1	17,3	5,7	110
	1,4/5,3	14,6/42,4 - 0,8/10,6			100				
22	PtCl ₂	B1 - Li ₂ CO ₃	1:4	H ₂	H ₂ O	20 3 1	25,1	4,1	105
	1,4/5,3	21,7/21,2 - 0,4/5,3			100				
23	PtCl ₂	D1 - Li ₂ CO ₃		H ₂	H ₂ O	20 4 1	9,5	10,6	130
	1,4/5,3	7/- - 0,4/5,3			100				
24	PtCl ₂	C1 - Li ₂ CO ₃		H ₂	H ₂ O	20 2 1	9,7	10,6	145
	1,4/5,3	7/- - 0,4/5,3			100				

Table 6: continuation 3

No.	Metal salt g/mmole	Tenside g/mmole	Metal salt/- tenside molar ratio	Reduction agent	Solvent ml	Reaction conditions T, t, h P, bar °C	isolated amount of product g	Metal content %	Water solubility in mg atom metal / l water
25	PICl ₂ 1,4/5,3	E1 - U ₂ CO ₃ 8,3/21,2 - 0,4/5,3	1:4	H ₂	H ₂ O 100	20 4 1 20 4 1	11,5	8,9	110
26	PICl ₂ 1,4/5,3	F1 - U ₂ CO ₃ 7,2/- - 0,4/5,3		H ₂	H ₂ O 200	20 3 1 20 3 1	13,7	6,8	110
27	PICl ₂ 1,4/5,3	B2 - U ₂ CO ₃ 7,2/21,2 - 0,4/5,3	1:4	H ₂	H ₂ O 100	20 3 1 20 3 1	10,8	9,1	105

- 31 -

C l a i m s

1. Process for producing tenside-stabilized colloids of mono- and bimetals of the groups VIII and Ib of the periodic system having particles sizes of 1-10 nm, characterized in that metal salts are reacted in the presence of strongly hydrophilic tensides selected from the group consisting of amphiphilic betaines, cationic tensides, fatty alcohol polyglycol ether, polyoxyethylene-carbohydrate-fatty alkylester and/or anionic tensides and/or amphiphilic sugar tensides, in THF, alcohols, or directly in water, with chemical reduction agents such as hydrides, hydrogen or alkali formate, between 0°C and 100°C at normal pressure, optionally by adding alkali carbonates and/or ammonium chloride, and that the precursors are isolated from the thus prepared solutions of >100 mg atom metal/l.
2. Process for producing carrier supported metal colloid catalysts by using preformed, tenside-stabilized mono- and bimetallic colloids of metals of the groups VIII and Ib of the periodic system according to claim 1, characterized in that the colloids stabilized by tensides are used in the form of solutions for adsorptive coverage of carriers.
3. Tenside-stabilized colloids of mono- and bimetals of the groups VIII and Ib of the periodic system having particles sizes of 1-10 nm, characterized by a surface area coverage with strongly hydrophilic tensides, selected from the group consisting of amphiphilic betaines, cationic tensides, fatty alcohol polyglycol ether, polyoxyethylene-carbohydrate-fatty alkylesters and/or anionic tensides and/or amphiphilic sugar

tensides, which are obtainable by chemical reduction with reduction agents such as hydrides, hydrogen or alkali formate, of metal salts in the presence of tensides between 0°C and 100°C at normal pressure, optionally by adding alkali carbonates and/or ammonium chloride, and isolation of the precursor from the thus prepared solutions of >100 mg atom metal/l.

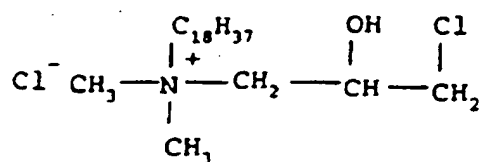
4. Colloids according to claim 3, characterized in that the strongly hydrophilic tensides are selected from particularly nonionic tensides having HLB-values of > 8.
5. Use of the tenside-stabilized colloids of mono- and bimetals, obtainable according to claims 1 and 2, as precursors for producing metal colloid-heterogeneous catalysts by adsorption from aqueous solution onto inorganic or organic carrier materials..
6. Use according to claims 1 to 5, characterized in that the metal colloids are used in concentrations of up to 25 percent per weight of metal content in relation to the total weight of the solution.
7. Use of the metal colloid-heterogeneous catalysts Pt-A-activated carbon, Pd-A-carbon, Pd/Pt-A-carbon, obtainable according to claim 5, for the partial oxidation of primary alcohol functionalities in carbohydrates.
8. Use according to claims 1 to 5, characterized in that carbon carriers, ceramic oxides, carbonates, sulfates or zeolites in the form of powders or formed bodies are used as carriers.
9. Use of the palladium colloid-A-carbon-catalysts, respectively, Pd-colloid-CaCO₃-catalysts, obtainable

- 33 -

according to claim 5, for the selective cis-hydrogenation of C-C- triple bonds.

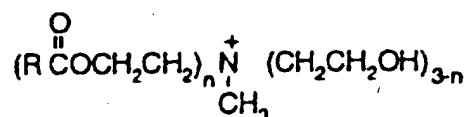
10. Use of the heterogeneous catalysts on oxides of the metal oxides of the lanthanoids, prepared according to claim 5, as carrier for the selective hydrogenation of benzene to cyclohexene.
11. Use of the rhutenium-lanthanoidoxide-heterogeneous catalysts, obtainable according to claim 10, for the selective hydrogenation of benzene to cyclohexene.
12. Mono- and bimetallic colloids (particle size 1-10 nm) from Cu, Ru, Rh, Pd, Ir, Pt, Ag, Ru/Fe, Pt/Co, Pt/Rh, Pt/Pd, Pt/Ir, Pt/Cu, Pt/Ru, Rh/Ir, Rh/Ru, Ru/Ir which are alkali-free stabilized hydrophilically with 3-(N,N-dimethyldodecyl ammonium)propane sulfonate, and being soluble in water at a concentration of > 100 mg atom metal/l.
13. Mono- and bimetallic colloids (particle size 1-10 nm) from Ru, Rh, Pd, Pt, Pt/Co, Pt/Ni, Pt/Ir, Pt/Cu, which are hydrophilically stabilized with lauryldimethyl carboxymethyl ammonium betaine, and being soluble in water at a concentration of > 100 mg atom metal/l.
14. Ru- and Pt-colloids (particle size 1-10 nm) which are hydrophilically stabilized with cocoamidopropyl betaines, and being soluble in water at a concentration of > 100 mg atom metal/l.
15. Platinum colloids (particle size 1-10 nm) which are hydrophilically stabilized with

- 34 -



and being soluble in water at a concentration of > 100 mg atom metal/l.

16. Platinum colloids (particle size 1-10 nm) which are hydrophilically stabilized with



R = alkyl radical of partially hydrogenated palm grease, and being soluble in water at a concentration of > 100 mg atom metal/l.

17. Mono- and bimetallic colloids (particle size 1-10 nm) from Ni, Co, Pt, Pt/Pd which are hydrophilically stabilized with polyoxyethylene laurylether, and being soluble in water at a concentration of > 100 mg atom metal/l.
18. Platinum colloids (particle size 1-10 nm) which are hydrophilically stabilized with polyoxyethylene sorbitan monolaurat, and being soluble in water at a concentration of > 100 mg atom metal/l.
19. Platinum colloids (particle size 1-10 nm) which are hydrophilically stabilized with Na-cocoamidoethyl-N-hydroxyethyl-glycinate, and being soluble in water at a concentration of > 100 mg atom metal/l.
20. Platinum colloids (particle size 1-10 nm) which are hydrophilically stabilized with alkylpolyglycoside, and

- 35 -

being soluble in water at a concentration of > 100 mg atom metal/l.

21. Carrier fixed heterogeneous metal colloid catalysts comprising mono- and bimetals of the groups VIII and Ib of the periodic system, obtainable by the use of solutions of preformed tenside-stabilized mono- or bimetal colloids of said metals by adsorptive coverage of said carriers.
22. Catalysts according to claim 21 comprising inorganic or organic carrier materials.
23. Catalysts according to claim 21, characterized in that the carrier materials comprise carbon carriers, ceramic oxides, carbonates, sulfates or zeolites in the form of powders or formed bodies.
24. Catalysts according to one or more of the claims 21 to 23 characterized by a coverage comprising oxides of lanthanoide elements, in particular lanthanum oxide.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 95/04803

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01J37/03 B01J37/02 B01J13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 147 841 (WILCOXON JESS P) 15 September 1992 see claim 1	1
X	DE,A,44 10 353 (YUKONG LTD) 29 September 1994 see page 3, line 65 - page 4, line 40	1-3,5,8, 21-23
X	EP,A,0 580 559 (TANAKA PRECIOUS METAL IND ;STONEHART ASS INC (US)) 26 January 1994 see claim 1	1,2
Y		7
Y	US,A,4 136 059 (JALAN VINOD M ET AL) 23 January 1979 see claim 1; example 1	7
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

7 May 1996

Date of mailing of the international search report

13.05.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo.nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Thion, M

INTERNATIONAL SEARCH REPORT

Application No
PCT/EP 95/04803

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>GB,A,212 035 (WALTER ALBERT PATRICK) 6 March 1924</p> <p>-----</p>	

INTERNATIONAL SEARCH REPORT

on patent family members

ial Application No

EP 95/04803

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5147841	15-09-92	NONE	
DE-A-4410353	29-09-94	JP-A- 7100380	18-01-95
EP-A-0580559	26-01-94	JP-A- 6031166	08-02-94
		DE-D- 69301074	01-02-96
		US-A- 5350727	27-09-94
US-A-4136059	23-01-79	CA-A- 1098890	07-04-81
		EP-A,B 0002651	27-06-79
		JP-C- 1232811	26-09-84
		JP-A- 54092588	21-07-79
		JP-B- 59005012	02-02-84
GB-A-212035		DE-C- 342094	
		DE-C- 434211	
		US-A- 1577188	16-03-26